1214361

PATENT SPECIFICATION (11) 1214361

DRAWINGS ATTACHED

(21) Application No. 31570/68 (22) Filed 2 July 1968

(23 Complete Specification filed 6 June 1969

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C4A 6

C1M V1K1 V1M V1K3B V2C1 V2C4 V2C7 V2C9 V2F1 V2F15 C2F19 V2F29 V2F33 V2F34 V2J3 V2K1 V2K3 V2K8 V2P

C3P 10C8B 10D1A 10S3 7C8B 7D1A

(54) IMPROVEMENTS IN PIGMENTS

SPECIFICATION NO. 1,214,361

INVENTOR: Reginald Walter Batchelor

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of HARRISON MAYER LIMITED, a British Company of Phoenix Chemical Works, Garth Street, Hanley, Stoke-on-Trent, Staffordshire.

THE PATENT OFFICE

R 1288/37/

ment produced by calcination at a temperature within the range of 1100—1350°C of a mixture of titanium dioxide with a barium compound which yields barium oxide on heating in the molar ratio Ba O. Ti O_2—Ba O. n Ti O_2 where n is a number up to 20, and nickel oxide or a compound which yields nickel oxide when heated, the amount of Ni O in the calcined mixture not exceeding 20% by weight.

The pigment has a strong yellow colour, with a maximum reflectance at a wave length of about 580 Mμ and has been tested ceramically as a glaze stain, a vitreous enamel stain and as an underglaze colour and found to be stable. It can also be employed as a yellow pigment for plastics in which application it has good chemical durability and light-fastness. The pigment can also be incorporated in paint.

A nickel-titanium-antimony yellow pigment is well known and is employed in similar applications. The pigment according to the invention, however, is a greener shade of yellow, and the cost of the materials required to manufacture it is only about half.

This difference in shade is shown by the spectrophotometric curves in the accompanying drawing, in which percentage reflectance is plotted as ordinates and wave length as abscissae. Curve A is that given by a conventional nickel-titanium-antimony pigment obtained by calcining a mixture of 20 parts by weight of

[Price

bright and tends to become dull at 15% Ni O. The preferred content of nickel oxide is 5—15% by weight irrespective of the ratio of Ba O to Ti O_2.

The yellow colour begins to appear weakly at a calcination temperature of 1150°C and intensity increases with increase in the temperature. We find that best results are obtained by firing at 1250—1300°C. If the mixture is calcined at a temperature above 1350°C the mass sinters to a hard lump which cannot easily be broken down.

In the following Examples the parts stated are parts by weight:—

EXAMPLE 1

The following materials were thoroughly mixed together and calcined at 1250°C for 1 hour:

Barium carbonate	38 parts
Titanium dioxide	62 „
Nickel oxide	10 „

when they yielded a bright yellow powder. This was washed with hot water and ground to pass a 200 mesh B.S.S. sieve in a ball mill, and then dried.

5 parts by weight of this powder were wet-milled together with 100 parts by weight of a white opaque glaze of the following composition:

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C3P 10C8B 10D1A 10S3 7C8B 7D1A

(54) IMPROVEMENTS IN PIGMENTS

(71) We, HARRISON MAYER LIMITED, of Phoenix Chemical Works, Garth Street, Hanley, Stoke-on-Trent, Staffordshire, a British Company, and REGINALD WALTER BATCHELOR, of 65 Walleys Drive, Basford, Newcastle-under-Lyme, Staffordshire, a British Subject,

do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention provides a novel yellow pigment produced by calcination at a temperature within the range of 1100—1350°C of a mixture of titanium dioxide with a barium compound which yields barium oxide on heating in the molar ratio Ba O. Ti O_2—Ba O. n Ti O_2 where n is a number up to 20, and nickel oxide or a compound which yields nickel oxide when heated, the amount of Ni O in the calcined mixture not exceeding 20% by weight.

The pigment has a strong yellow colour, with a maximum reflectance at a wave length of about 580 Mμ and has been tested ceramically as a glaze stain, a vitreous enamel stain and as an underglaze colour and found to be stable. It can also be employed as a yellow pigment for plastics in which application it has good chemical durability and light-fastness. The pigment can also be incorporated in paint.

A nickel-titanium-antimony yellow pigment is well known and is employed in similar applications. The pigment according to the invention, however, is a greener shade of yellow, and the cost of the materials required to manufacture it is only about half.

This difference in shade is shown by the spectrophotometric curves in the accompanying drawing, in which percentage reflectance is plotted as ordinates and wave length as abscissae. Curve A is that given by a conventional nickel-titanium-antimony pigment obtained by calcining a mixture of 20 parts by weight of antimony trioxide, 62 parts by weight of titanium dioxide and 12 parts by weight of nickel carbonate. Curve B is that given by the product of Example 1 below.

The yellow colouration is most intensive in the range of high titania, particularly around the molar ratio Ba O . 4 Ti O_2. The yellow colour is obtained with a very small amount of Ni O and increases in brightness and intensity with increase in the Ni O content to a maximum at 10% Ni O. At higher contents of Ni O the yellow becomes darker and less bright and tends to become dull at 15% Ni O. The preferred content of nickel oxide is 5—15% by weight irrespective of the ratio of Ba O to Ti O_2.

The yellow colour begins to appear weakly at a calcination temperature of 1150°C and intensity increases with increase in the temperature. We find that best results are obtained by firing at 1250—1300°C. If the mixture is calcined at a temperature above 1350°C the mass sinters to a hard lump which cannot easily be broken down.

In the following Examples the parts stated are parts by weight:—

EXAMPLE 1

The following materials were thoroughly mixed together and calcined at 1250°C for 1 hour:

Barium carbonate	38 parts
Titanium dioxide	62 „
Nickel oxide	10 „

when they yielded a bright yellow powder. This was washed with hot water and ground to pass a 200 mesh B.S.S. sieve in a ball mill, and then dried.

5 parts by weight of this powder were wet-milled together with 100 parts by weight of a white opaque glaze of the following composition:

SiO_2	55	parts by weight
Al_2O_3	12	„ „ „
CaO	5	„ „ „
Na_2O	6	„ „ „
ZnO	4	„ „ „
B_2O_3	9	„ „ „
ZrO_2	9	„ „ „

When applied to a ceramic biscuit tile and fired at 1050°C this preparation produced a glossy primrose yellow glazed surface.

EXAMPLE 2

The following materials were thoroughly mixed together and fired for 1 hour at a temperature ranging from 1200—1300°C.

Barium carbonate	30 parts
Titanim dioxide	60 „
Nickel carbonate	10 „

A bright yellow powder was produced, which was washed, ground to pass a 200 mesh B.S.S. sieve in a ball mill, dried and further ground to an average size of 0.5 micron as determined by electron micrographs. This powder was incorporated at various percentages from 0.5 to 3.0% by weight in polyester resins, polyethylene and polyvinyl chloride plastisols. In all cases a bright yellow opaque product was produced. On diluting with titanium dioxide, various shades of primrose and deep ivory were produced. The coloured plastic samples so made were exceptionally stable to light and to acid and alkaline solutions.

EXAMPLE 3

The following mixture of ingredients was fired at 1250°C for 1 hour to produce a bright yellow powder:

Barium carbonate	28 parts
Titanium dioxide	55 „
Nickel phosphate	17 „

After washing and grinding 7 parts by weight of this powder were added to 100 parts by weight of a conventional white opaque vitreous enamel, and when fired on iron, produced a pleasing primrose yellow coating.

The calcine was also sprayed on to a ceramic plate, and covered with a conventional transparent glaze of the following molecular composition:—

0.25	PbO		3.6 SiO_2
0.30	Na_2O	0.4 Al_2O_3	
0.45	CaO	0.5 B_2O_3	

After firing at 1080°C, a bright yellow glossy colour was imparted to the portion of the ceramic plate so treated.

EXAMPLE 4

The following mixture was fired at 1250°C for 1 hour and produced a bright yellow product.

Barium carbonate	71 parts
Titanium dioxide	29 „
Nickel oxide	10 „

After washing with hot water the product was ground to pass a 200 mesh B.S.S. sieve and dried.

10 parts by weight of this powder and 10 parts by weight of zirconium silicate were ground together with 100 parts by weight of a leadless glaze whose composition corresponded to the following molecular formula.

0.309	Na_2O		
0.195	K_2O	0.482 Al_2O_3	2.87 SiO_2
0.496	CaO	0.474 B_2O_3	

The stained glaze so produced was sprayed on to white ceramic tile and fired at 1060°C for 1 hour to produce a pleasing ivory glazed tile.

EXAMPLE 5

The following mixture was ground together and fired at 1250°C for 1 hour.

Barium carbonate	27.3 parts
Titanium dioxide	62.6 „
Nickel carbonate	10.1 „

A brilliant yellow powder was produced, which when finely ground and incorporated in a polyester resin at 3 parts by weight to 100 of resin gave a pleasing yellow colouration.

In Examples 1—3 the molar ratio of BaO and TiO_2 is approximately 1:4, and in Example 4 it is 1:1. Example 5 yields a product of molar ratio 2 NiO. 3 BaO. 17 TiO_2.

A number of the pigments made experimentally in accordance with the invention have been examined by X-ray diffraction and in all cases a predominant lattice formation corresponding to a distorted "Priderite" type structure of composition close to 2 NiO. 3 BaO. 17 TiO_2 has been found. Priderite is a mineral quoted as having the composition $(K, Ba)_{1.33}(TiFe)_8O_{16}$.

WHAT WE CLAIM IS:—

1. A yellow pigment produced by calcination at a temperature within the range of 1100—1350°C of a mixture of titanium dioxide with a barium compound which yields barium oxide on heating in the molar ratio Ba O. Ti O_2—Ba O. n Ti O_2, where n is a number up to 20, and nickel oxide or a compound which yields nickel oxide when heated, the amount of Ni O in the calcined mixture not exceeding 20% by weight.

2. A pigment as claimed in claim 1, in

which the content of Ni O in the calcined mixture is 5—15% by weight.

3. A pigment as claimed in claim 1 or claim 2, in which the molar ratio of barium oxide to titanium dioxide is 1 to 4.

4. A method of making a pigment as claimed in any preceding claim in which the mixture is calcined at a temperature of 1250—1300°C.

5. A pigment as claimed in claim 1, substantially as described herein with reference to any of the foregoing Examples.

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1214361 COMPLETE SPECIFICATION

1 SHEET *This drawing is a reproduction of the Original on a reduced scale*